National Institute of Standards and Technology
Chemical Science and Technology Laboratory

Basic Radiation Chemistry

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Radiation Chemistry

Radiation chemistry **is the study of the chemical effects of high energy, ionizing radiation.**

High energy radiation includes electromagnetic radiation (X-rays and γ-rays), and particles (α-particles, β-particles or electrons, protons and neutrons).

Radiation chemistry should not be confused with *radiochemistry*, which deals with the chemistry of radioactive elements, or with *nuclear chemistry*, which is concerned with nuclear transformations, particularly fission product and transuranium elements.

It is also distinct from *photochemistry*, which covers the chemical effects of light, especially ultraviolet (UV) light, which is not considered ionizing radiation. The boundary is not sharp, and can be taken as the energy of the most firmly bound outer electrons, i.e., 30 eV (5×10^{-18} Joule) per molecule corresponding to a wavelength of 40 nm in the vacuum-ultraviolet (starting with 200 nm).

Fundamental Studies

Fundamental studies in radiation chemistry aim to identify the various species formed in particular systems and to understand the physical processes by which they arise.

The amounts formed for a given dose of radiation are measured.

Then the chemistry of the species in their reactions with each other and with other compounds present is studied.

This involves investigation reaction kinetics and mechanisms, and of intermediates through the final, stable end-products.

Ionizing Radiation

The principal characteristic of ionizing radiation is that it has sufficient energy to break any chemical bond and to cause ionization in all material.

Whenever the energy of a particle or photon exceeds the ionization potential of a molecule, a collision with the molecule might lead to ionization. Gas phase ionization potentials of molecules range between 8 eV and 13 eV (1 eV = 1.6×10^{-19} Joule).

Interaction of Ionizing Radiation with Matter

1. Charged Particles

2. Photons

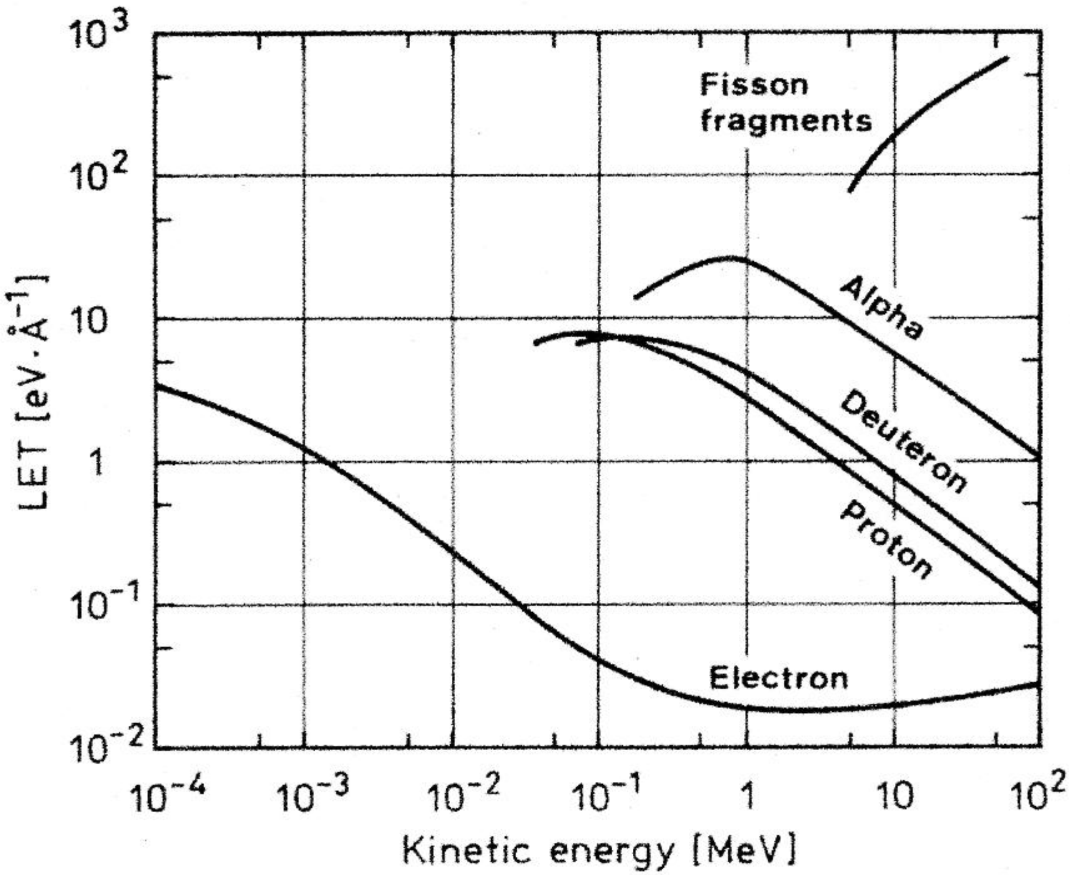
3. Neutrons

4. Electronic excitation

5. Spur model

6. Radiation chemical yield, “the *G* value”

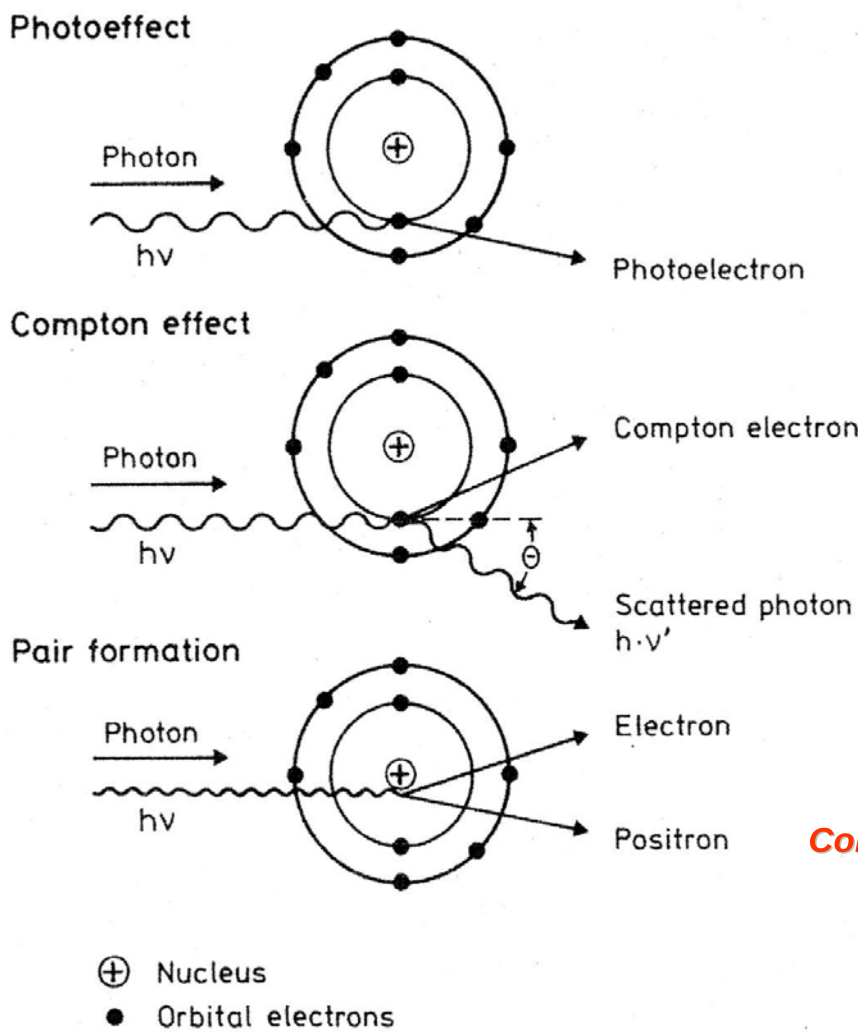
Interaction of Ionizing Radiation with Matter
Charged Particles



Specific energy loss as a function of energy for the stopping of various particles in water

LET (Linear energy transfer; d*E*/d*x*)

Interaction of Ionizing Radiation with Matter
Photons



hν < 50 keV

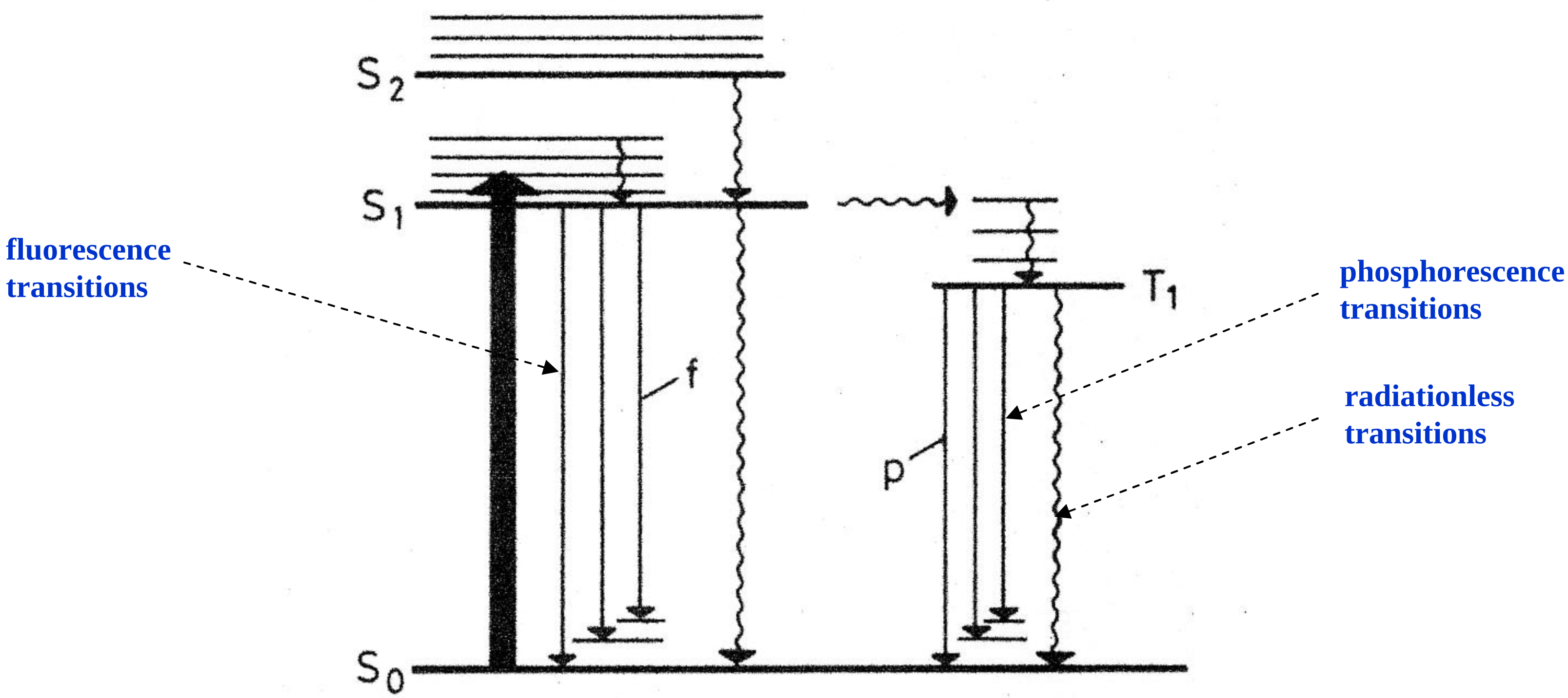
hν ≈ 50 keV – 20 MeV

hν ≈ 20 MeV – 30 MeV

Conversion of energy into matter

Electronic excitation

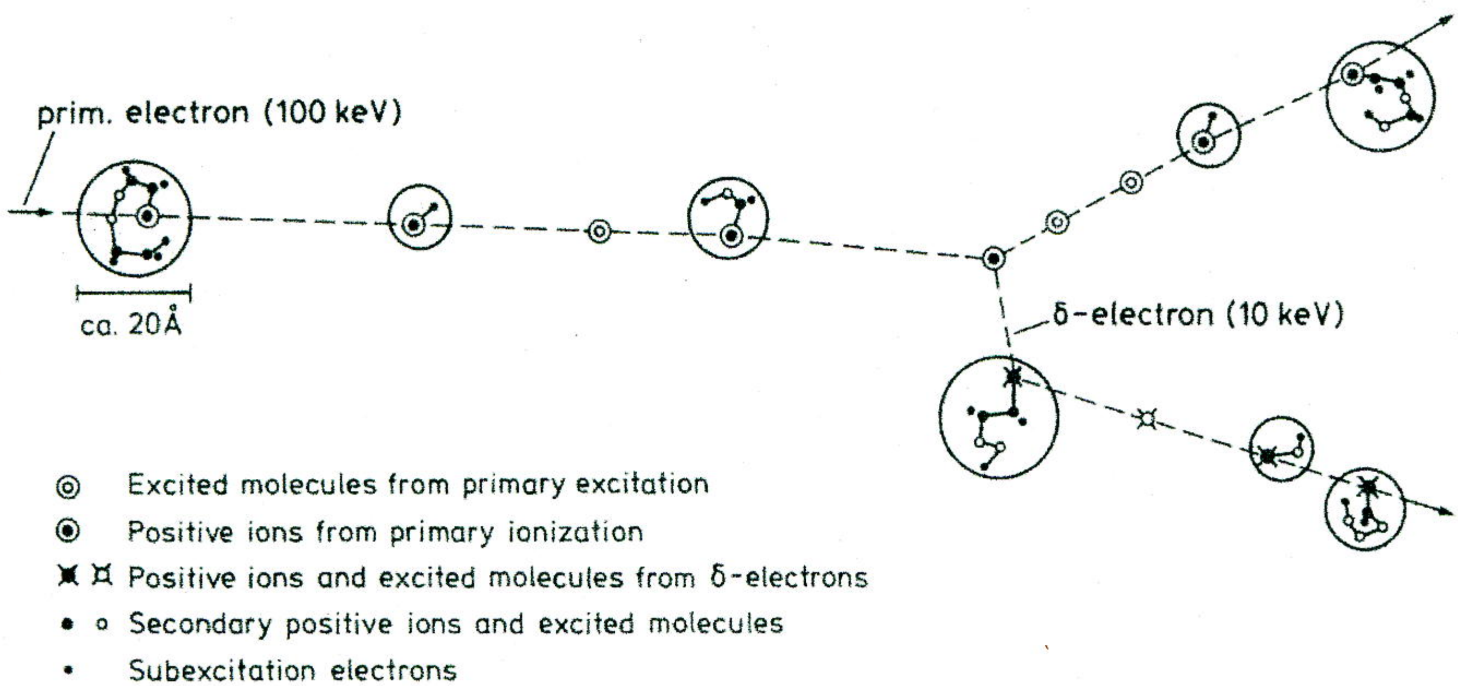
Diagram of some electronic and vibrational transitions



S_0: Ground state
S_1: The first excited singlet state (spin of two electrons are antiparallel)
S_2: The second excited singlet state (spin of two electrons are antiparallel)
T_1: The first excited triplet state (spin of two electrons are parallel)

Spur Model

When an ionizing particle, e.g., a 100 keV electron, passes through absorbing matter, energy is not deposited uniformly, but in small packages called “spurs.”



The G-value

In *photochemistry*, the yield of a photochemical reaction is expressed as *the quantum yield*:
"The ratio of the number of molecules divided by the number of quanta absorbed".

In *radiation chemistry*, the energy of the photon or the particles exceeds the binding energy of an electron (normally $<$13 eV) and a high-energy quantum, e.g., a ^{60}Co γ-quantum, which equals to 1.32 MeV, can no longer be absorbed by one single molecule.

Nevertheless, it is useful to define a similar quantity:
"The ratio of the number of product molecules formed in an irradiated sample to the amount of energy deposited in it".

This is called "*the G-value*" and is expressed in the units "molecules/100 eV", which is equivalent to "1.036×10^{-7} mol J^{-1}" in SI units.

This energy-related value is very useful if chemical effects of sparsely and densely ionizing radiation have to be compared.

Units commonly used in radiation research

Radiation-physical quantities	*Unit*			*Conversion to other systems*
Activity	bequerel	Bq	(s^{-1})	1 curie (Ci) = $3{\cdot}7 \times 10^{10}$ Bq
Absorbed dose	gray	Gy	($J\ kg^{-1}$)	1 rad = 0·01 Gy
Dose equivalent	sievert	Sv	($J\ kg^{-1}$)	1 rem = 0·01 Sv
Energy	joule	J	(N m)	1 eV = $1{\cdot}60 \times 10^{-19}$ J 1 cal = 4·18 J
Power	watt	W	($J\ s^{-1}$)	
Electric charge	coulomb	C		
Radiation-chemical yield	*G* value		($mol\ J^{-1}$)	1 molecule $(100\ eV)^{-1} \triangleq 1{\cdot}036 \times 10^{-7}\ mol\ J^{-1}$
Exposure			($C\ kg^{-1}$)	1 röntgen = $2{\cdot}58 \times 10^{-4}\ C\ kg^{-1}$
Dose rate			($Gy\ s^{-1}$)	

Effects of Ionizing Radiation

1. **Direct effect**

   Ionization, excitation

2. **Indirect effect**

   Reactions of the species formed from the solvent with the solute

Radiation chemistry of water

$$H_2O \xrightarrow{\text{ionizing radiation}} H_2O^{+\bullet} + e^-$$ *ionization*

$$H_2O \xrightarrow{\text{ionizing radiation}} H_2O^{*}$$ *excitation*

Time scale 10^{-16} s

Free radical

A free radical is any species capable of independent existence (*hence term "free"*) that contains one or more unpaired electrons

An unpaired electron is one that occupies an atomic or molecular orbital

Radiation chemistry of water

$$H_2O^* \longrightarrow \boxed{H^\bullet} + \boxed{{}^\bullet OH}$$

$$H_2O^{+\bullet} + H_2O \longrightarrow H_3O^+ + \boxed{{}^\bullet OH}$$

$$e^- + n\,H_2O \longrightarrow \boxed{e_{aq}^-}$$

$$e_{aq}^- + H^+ \longrightarrow \boxed{H^\bullet}$$

k = 5 x 10^9 M^{-1} s^{-1} – 3 x 10^{10} M^{-1} s^{-1}

Time scale 10^{-16} – 10^{-7} s

$A + B \rightarrow C + D$

Rate = $-d[A]/dt = k[A][B]$ "second-order reaction"

k = rate constant (M^{-1} s^{-1})

Radiation chemistry of water

$$H^{\bullet} + H^{\bullet} \longrightarrow \boxed{H_2}$$

$$e_{aq}^{-} + e_{aq}^{-} \xrightarrow{H_2O} \boxed{H_2} + 2\ OH^{-}$$

$$^{\bullet}OH + {}^{\bullet}OH \longrightarrow \boxed{H_2O_2}$$

k = 5 x 10^9 M^{-1} s^{-1} – 3 x 10^{10} M^{-1} s^{-1}

Radiation chemistry of water

$$H^{\bullet} + {}^{\bullet}OH \longrightarrow \boxed{H_2O}$$

$$e_{aq}^{-} + {}^{\bullet}OH \longrightarrow \boxed{OH^{-}}$$

$$H^{+} + OH^{-} \longrightarrow \boxed{H_2O}$$

$$e_{aq}^{-} + H_2O_2 \longrightarrow \boxed{{}^{\bullet}OH} + OH^{-}$$

k = 5 x 10^9 M^{-1} s^{-1} – 3 x 10^{10} M^{-1} s^{-1}

Restricted radical sources

$$e_{aq}^{-} + N_2O \longrightarrow {}^{\bullet}OH + N_2 + OH^{-}$$

$$k = 9.1 \times 10^{9}\ M^{-1}\ s^{-1}$$

The system consists of 90% $^{\bullet}OH$ and 10% $H^{\bullet}$

$[N_2O] = 2.2 \times 10^{-2}$ M *saturated*

$[O_2] = 2.2 \times 10^{-3}$ M *saturated*

Radiation chemistry of water
Effect of oxygen

$$e_{aq}^{-} + O_2 \longrightarrow \boxed{O_2^{\bullet -}}$$ *superoxide radical*

$$H^{\bullet} + O_2 \longrightarrow \boxed{HO_2^{\bullet}}$$ *hydroperoxyl radical*

$$HO_2^{\bullet} \rightleftharpoons H^{+} + O_2^{\bullet -}$$ $pK_a = 4.7$

$$^{\bullet}OH + HCO_2^{-} \longrightarrow CO_2^{\bullet -} + H_2O$$

$$CO_2^{\bullet -} + O_2 \longrightarrow CO_2 + \boxed{O_2^{\bullet -}}$$

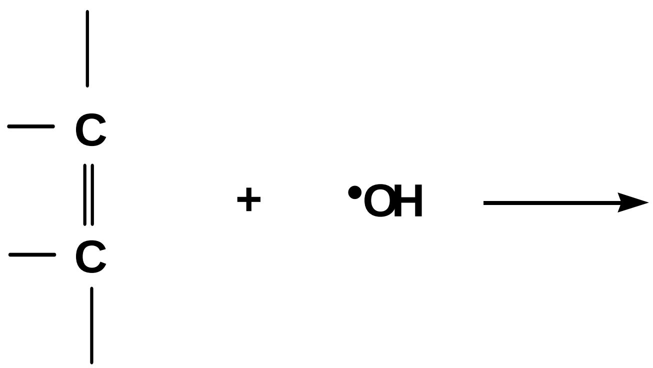
Radiation chemistry of water

$$H_2O \xrightarrow{\text{ionizing radiation}} {}^{\bullet}OH,\ e_{aq}^{-},\ H^{\bullet},\ O_2^{\bullet -},\ H_2O_2,\ H_2$$

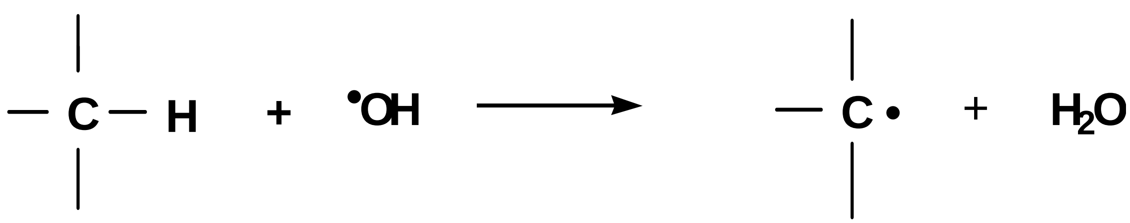
^{60}Co γ-irradiation *G*-values (number of species/100 eV) of water radicals and molecular products

	N_2	N_2O	N_2O/O_2	O_2
$^{\bullet}OH$	2.7	5.4	5.4	2.7
$H^{\bullet}$	0.55	0.55	–	–
e_{aq}^{-}	2.7	–	–	–
$HO_2^{\bullet}/O_2^{\bullet-}$	–	–	0.55	3.2
H_2O_2	0.7	0.85	?	?
H_2	0.45	0.45	0.45	0.45

Reactions of water radicals with substrates

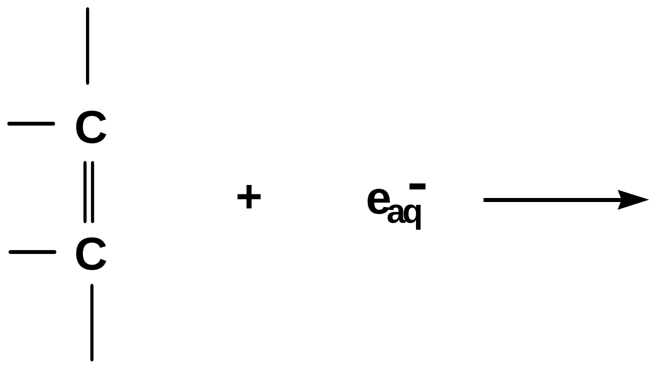


addition

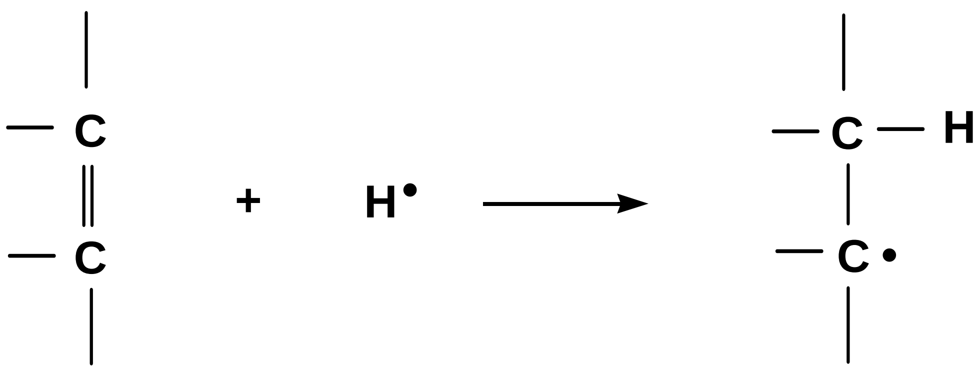


abstraction

Reactions of water radicals with substrates



addition

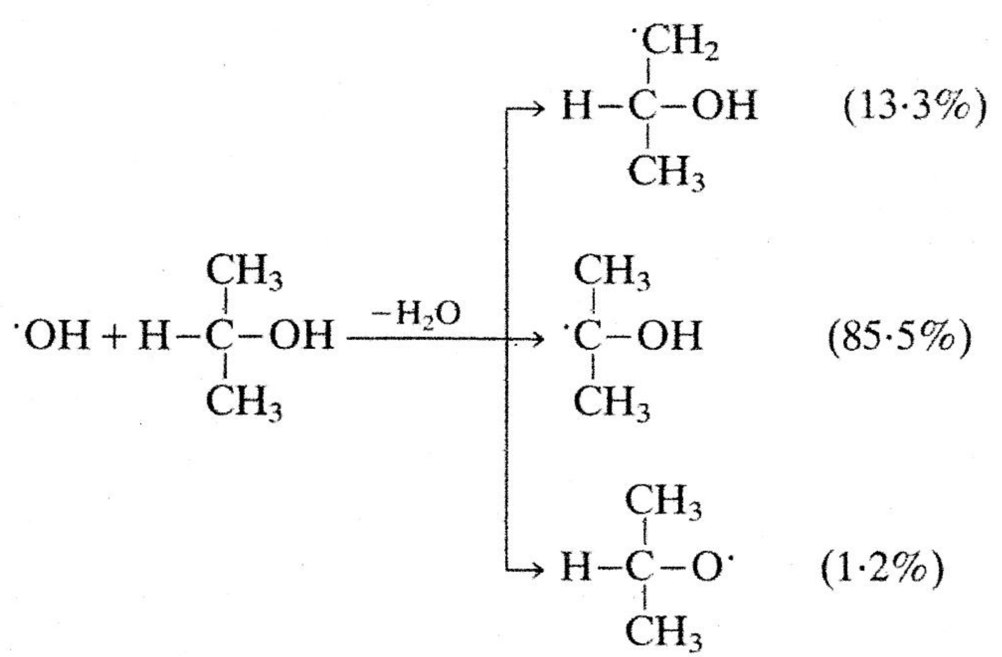


addition

Reactions of water radicals with substrates

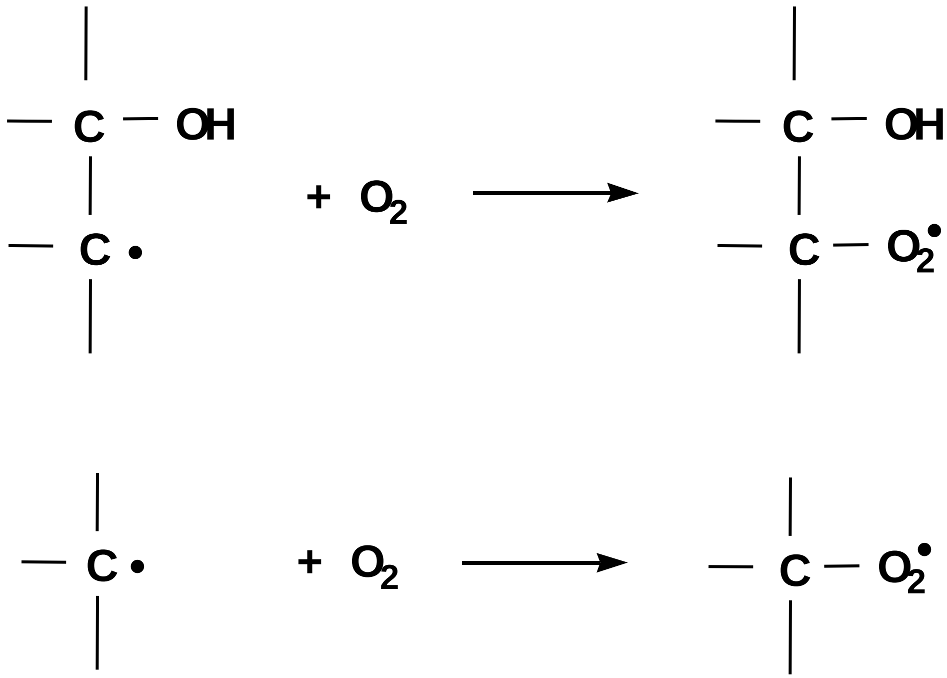
$$Ag^+ + {}^{\bullet}OH \longrightarrow (AgOH)^+$$

$$(AgOH)^+ + H^+ \rightleftharpoons Ag^{2+} + H_2O$$



$k = 2 \times 10^{10}\ M^{-1}\ s^{-1}$

Reactions of oxygen with C-centered radicals



$k = 2 \times 10^{9}\ M^{-1}\ s^{-1}$

Oxidative Stress

- Oxidative stress refers to the situation of a serious imbalance between production of reactive oxygen and nitrogen species, and antioxidant defenses.

- Oxidative stress is a disturbance in the prooxidant-antioxidant balance in favor of the former, leading to potential damage, called ***"oxidative damage".***

- Oxygen is toxic. It is reduced in the electron transport chain in mitochondria by cytochrome oxidase.

$$O_2 \xrightarrow{e^-} O_2^{\bullet -} \xrightarrow{e^-} H_2O_2 \xrightarrow{e^-} {}^{\bullet}OH \xrightarrow{e^-} H_2O$$

Metal ion-catalyzed Haber-Weiss reaction

$$O_2^{\bullet -} + Fe(III) \longrightarrow O_2 + Fe(II)$$

$$H_2O_2 + Fe(II) \longrightarrow {}^{\bullet}OH + OH^{-} + Fe(III)$$

$$O_2^{\bullet -} + H_2O_2 \longrightarrow {}^{\bullet}OH + OH^{-} + O_2$$

k = 0.13 M^{-1} s^{-1}

Targets in radiation biology

The main target for radiation-induced cell killing is DNA

1. The size of the target is important. The nucleus constitutes a large part the cell.

2. DNA molecule is unique and has low redundancy, and each molecule is more vulnerable than highly redundant compounds such as lipids.

3. Chromosomal damage parallels lethality.

4. Sensitivity of many related cells and organisms parallels the DNA content.

5. Incorporation of radioactive molecules such as ^{3}H-thymine into DNA leads to very efficient cell killing.

6. Incorporation of base analogues such as 5-bromouracil into DNA increases the sensitivity to ionizing radiation.

7. Cell killing shown to be associated with structural damage to DNA such as strand breaks, base damage, chromosome damage.